SPECTROSCOPIC CHARACTERIZATION OF ARGONNE PREMIUM COALS AND SHORT RESIDENCE TIME LIQUEFACTION PRODUCTS

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ABSTRACT

Illinois No. 6 (high volatile bituminous) , Pittsburgh No. 8 (bituminous), Wyoming Subbituminous, Pennsylvania Upper Freeport (medium volatile bituminous) and Pocahontas #3 (low volatile bituminous) coals from the Argonne Premium Coal Sample Program were heated in tetralin for 10 minutes at 430 ±5° C. The products were examined by gel permeation chromatography and ^{13}C NMR spectroscopy. Yields for conversion of the coals to THF-soluble products were determined. Yields and GPC characteristics of products from direct extraction of the coals with THF were determined. The most reactive coal in this group, based on conversion to products below MW 600, appears to be Wyoming subbituminous.

INTRODUCTION

The availability of pristine coal samples from the Argonne Premium Coal Program now makes possible the meaningful comparison of experimental results of spectroscopic studies and reactions between laboratories. In previous work with medium-rank coals, we have examined the structural evolution of thermal degradation products by NMR and gel permeation chromatography (GPC) techniques, and we have characterized the processes of hydrogen transfer and exchange under liquefaction conditions using deuterium labeling techniques(1-3). In this paper we present results of a study of the molecular weight distributions of products liberated from a short (10 minute) exposure of five of the premium coals to thermal decomposition in tetralin at 430 °C, and results of ^{13}C NMR characterization of the fractionated products.

EXPERIMENTAL

Coals. The five coals examined in this study were Pennsylvania Upper Freeport medium volatile bituminous coal (Penn UF), coal ID 101; Wyoming subbituminous coal (WYO), coal ID 201; Illinois No. 6 high volatile bituminous (Ill #6), coal ID 301; Pittsburgh #8 bituminous coal (Pitt #8), coal ID 401; and Pocahontas

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#3 low volatile bituminous coal (Poc #3), Coal ID 501.

Extraction of Coals with THF. The five coals (4-5 g each) were washed with three 100 mL portions of tetrahydrofuran (THF). The THF solution was filtered through a 0.45 micron Millipore type FH filter, concentrated, weighed, and examined by GPC and NMR.

Reactions of Coals with Tetralin. The reactions of the coals with tetralin were carried out in 3-mL stainless steel vessels described previously.[1] Tetralin (2 mL) and coal (1 g) were added, and the tube was heated for 10 minutes at 430±5 °C in a Tecam SBS-4 fluidized sand bath. The tubes were opened and washed out with THF. The THF solution and solids were filtered with a 0.45-micron type FH Millipore filter. The residue was air dried and weighed. The THF solution containing the coal products and reaction solvent (tetralin and naphthalene) were concentrated on a rotary evaporator to ca. 20 mL and pipetted into ca. 400 mL of hexane, resulting in the precipitation of brown flakes of the coal product. The THF-soluble, hexane-insoluble product (preasphaltenes and asphaltenes (P+A)) was weighed and examined by GPC and NMR spectroscopy. Occasionally, incomplete removal of tetralin and naphthalene occured. In these cases, the P+A fraction was redissolved in THF and reprecipitated from hexane. THF oxidation products were occasionally encountered, and were removed by precipitation of a THF solution of the P+A fraction by adding ca. 5-ml of the THF solution to about 100 mL water, which removes the water-soluble THF-associated impurities. For examination of the whole coal reaction mixtures by GPC, reaction tubes were washed out with THF, filtered, and examined directly by GPC.

Gel Permeation Chromatography of P+A, Whole Reaction Mixtures and THF Extracts. Gel permeation chromatography was carried out using one 500Å and one 100Å Waters Associates μStyragel® column in series, eluting with THF at a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards from 600-17500 MW and with a variety of low molecular weight compounds below MW 400.

^{13}C NMR Spectroscopy of Preasphaltenes + Asphaltenes (P+A). ^{13}C NMR spectra of the THF-soluble P+A fractions were determined with a Varian VXR-300 operating at 75 MHz. Approximately 250 mg of P+A fraction was dissolved in 3.0 mL THF-d_8 containing 0.1 M $Cr(acac)_3$. Spectra were acquired using a 90° pulse, 0.8-s acquisition time and a 3-s pulse delay with inverse gated decoupling. The use of 3% $Cr(acac)_3$ with inverse gated decoupling has been reported(4) to produce quantitative results for SRC-II liquids with negligible change in aromaticity (f_a) for pulse delays beyond 4 seconds, and an increase in measured f_a of less than 2% between pulse delays of 2 and 5 seconds. To obtain aromatic/aliphatic ratios, the integral of the 50-10 ppm region obscured by the upfield THF-d_8 multiplet was corrected using the integral of the downfield 67.4 ppm THF peak and a carefully determined integral ratio of the two multiplets of the spectrum of a solution of $Cr(acac)_3$ in THF-d_8. The values of f_a must be considered qualitative since the error for this procedure is probably 5-7%, while the error in the distribution in aromatic structure is lower.

RESULTS AND DISCUSSION

Direct extraction of the coals (Table I) produced 2-12% of THF-soluble product. Ill #6 is unique in its high solubility, whereas the other coals are

normal, exhibiting 2-4% solubility. The bulk of the directly extractable material clearly is of low molecular weight, with 60-90% below MW 600. Ill #6 and Pitt #8 give noticeably greater amounts of material above MW 600 than the other coals (Figure 1).

Reaction of the coals with tetralin for 10 minutes at 430° C produced yields varying from 3% for Pocahontas #3 to 56% for Pittsburgh #8. The yields from the 10-minute reactions are qualitatively in agreement with rank for the various coals. Total conversions are higher for Wyoming subbituminous, Pittsburgh #8, and Illinois #6. Notice in Table II that while Wyoming subbituminous exhibits the highest conversion, it produces only 25% preasphaltenes and asphaltenes. This means that up to 50% of Wyoming subbituminous is converted to hexane solubles (transfer loss and loss of volatiles is included in this upper estimate), making the Wyoming subbituminous by far the most readily converted coal in this group. The difference between conversion and P+A (%) in Table II is the yield of hexane solubles plus transfer loss and water loss, etc. Thus, hexane solubles may be produced in up to 8% (Penn UF), 17%(Poc #3), 19%(Pitt #8), 15%(IL #6) and 50%(Wyo Sub).

GPC data of Table III show that the bulk of THF-soluble products from all coals at short reaction times consists of material below 600 nominal molecular weight. The effectively inert Poc #3 produced primarily low molecular weight materials at both 10 and 40-minute reaction times. The P+A fractions all exhibit significant amounts of higher molecular weight material (Table IV), consistent with the expected characteristics of THF-solubility. Among the high yielding coals, Pitt 8, Wyo Sub, and Ill #6, the P+A fraction of Wyo sub (Table IV) shows the greatest amount of product below MW 600, consistent with the much greater apparent yield of hexane-solubles discussed above for Wyoming subbituminous. GPC data for extracts of raw coals, total reaction mixtures, and preasphaltene + asphaltene subfractions are depicted in Figure 1.

^{13}C FTNMR spectra of P+A fractions determined for the five coal extracts are presented numerically in Table V. THF solubility and hexane solubility tends to produce material of high polarity and rather similar NMR characteristics in the preasphaltene + asphaltene subfraction. The ranges of Table V correspond roughly to phenolic and aryl ether CO (168-148 ppm), substituted aryl C (148-129.5 ppm) and protonated aryl carbon (129.5-110 ppm), the latter group including protonated aryl carbon adjacent to aryl CO structure(5). Within the range of probable error, Table V results indicate higher aryl oxygen content for IL #6, Wyo Sub, and Pitt #8 than for Penn UF and Poc #3, and higher ring substitution for Poc #3.

The results of this paper provide quantitative data for estimation of the amount and structural distribution of products from short residence time liquefaction of the Argonne Premium Coals. A more detailed spectroscopic study of the organic structure of the Argonne coals is presently underway.

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Table I. Direct Extraction of Coals with THF

Coal	Wt. Coal Extd.	Wt. Extract	Wt. %
Ill #6	4.11 g	0.50 g	12%
Penn UF	4.36 g	0.07 g	2%
Wyo Sub	3.97 g	0.12 g	3%
Pitt #8	3.07 g	0.13 g	4%
Poc #3	4.77 g	0.10 g	2%

Table II. Asphaltene + Preasphaltene Yields from Coals[a]

Coal	Wt. Coal	Wt. Residue	Wt. P+A	%P+A	Conversion[b]
Penn UF	5 g	3.1 g	1.5 g	30%	38%
Poc #3	1 g	0.8 g	0.03 g	3%	20%
Poc #3[c]	3.5 g	2.0 g	0.6 g	17%	43%[c]
Pitt #8	4 g	1.0 g	2.24 g	56%	75%
Wyo Sub	4 g	1.0 g	1.0 g	25%	75%
Ill #6	4 g	1.7 g	1.0 g	43%	58%

[a] 10 minutes, 430 ± 5 °C.
[b] based on recovered coal ((Wt. Coal-Wt. Residue)/Wt. Coal), includes transfer losses, hexane-soluble products not included in P+A, and water losses.
[c] 40 minutes, 430 ± 5° C

Table III. GPC Data For THF-Soluble Products of Coal-Tetralin Unfractionated Reaction Mixtures

Coal	Area % MW Above 8500	Area % MW 8500-600	Area % MW Below 600
Ill #6	3.9	17.3	78.8
Ill #6[a]	0.3	13.2	86.5
Pitt#8	5.9	35.0	59.1
Penn UF	1.0	28.1	70.9
Wyo Sub	0.6	25.3	74.1
Poc #3	0.5	7.8	91.7
Poc #3[b]	0.6	11.0	88.4

[a] Coal was pre-extracted with THF before reaction
[b] 40-minute reaction time

Table IV. GPC Data for P+A Fractions from Premium Coals

Coal	Area % MW above 8500	Area % 8500-600	Area % Below 600
Ill #6	3.4	38.6	58
Pitt #8	5.6	52.8	41.5
Penn UF	7.2	44.0	48.7
Wyom Sub	3.1	31.3	65.6
Poc #3	3.2	40.3	56.4
Poc #3[a]	0.7	13.7	85.7

[a]40-minute reaction time

Table V. ^{13}C Spectroscopic results from P+A fractions

Coal	Distribution of Aromatic C %, ppm range			Aromaticity[a],%
	168-148	148-129.5	129.5-110	
Ill #6	10	44	46	81
Wyo Sub	12	41	47	76
Poc #3	7	55	38	ND
Pitt #8	10	43	47	80
Penn UF	7	34	59	70

[a]Estimated error ±5%

Table VI. GPC Data of THF Extracts of Premium Coals

Coal	Area % MW Above 8500	Area % MW 8500-600	Area % MW Below 600
Ill #6	1.6	30.6	67.9
Pitt #8	5.1	31.9	63.1
Penn UF	0.2	10.9	89.0
Wyo Sub	0.4	7.7	92.0
Poc #3	0.1	9.6	90.0

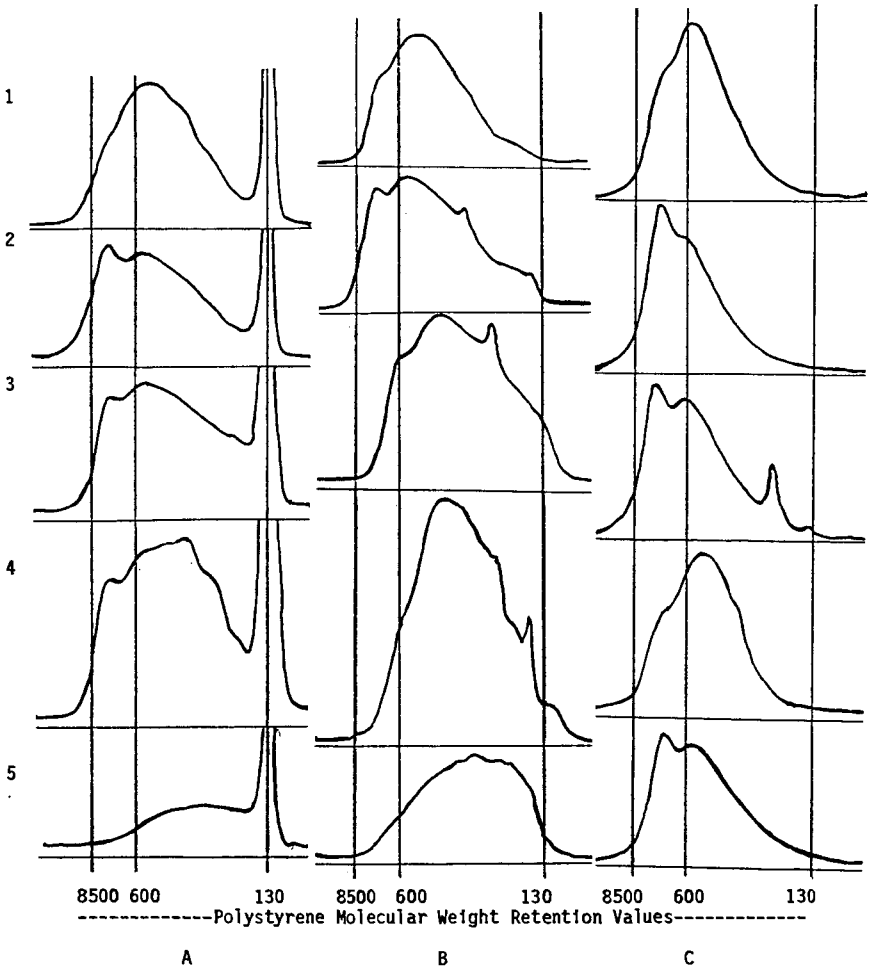

Figure I. Gel Permeation Chromatography Traces for A) Unfractionated Coal/Tetralin Reaction Mixtures; B) Products of THF extraction of the raw coals, and C) THF-Soluble, Hexane-insoluble Products (Preasphaltenes and Asphaltenes). The coals are Row 1, Illinois #6; Row 2, Pittsburgh #8; Row 3, Pennsylvania Upper Freeport; Row 4, Wyoming Subbituminous; Row 5, Pocahontas #3